N64-19223*

22p

CODE-1

title
STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

3RD QUARTERLY REPORT, 2 Jan - 31 Mar 1964

M. L. Kronenberg 1 April, 1964 22p refs

Technical Management
Auxiliary Power Generation Office
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio
Mr. W. J. Nagle

NASA Contract NAS3-2752

Period Covered: January 2 - March 31, 1964

NASA CR-54031 OTS $2.60 ph

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UNION CARBIDE CORPORATION
DEVELOPMENT DEPARTMENT
PARMA RESEARCH LABORATORY
PARMA, OHIO Parma Research Lab.

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Prepared by

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1.0 PURPOSE

This investigation is concerned with what effect the modification of the gas-electrolyte interface will have on the performance of fuel cell electrodes. The interface will be disturbed by electrical and mechanical pulses over a wide range of frequencies.

Hydrophobic and hydrophilic electrodes will be used in this investigation.

2.0 ABSTRACT

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There were no significant performance differences between cells operating on interrupted d. c. or a. c. superimposed on d. c. at frequencies from 20 cycles to 20 kilocycles per second and control cells operating at continuous d. c. The peak value of the superimposed a. c. was less than the d. c. level.

Improvement in the average performance of thin, composite cells up to 100 mv at 150 ma/cm^2 was noted when electrodes were subjected to heavy discharge pulses of short duration. Except for "breaking-in" phenomena the effect has been observed only at the anode and in general is most pronounced for anodes with more than 100 mv polarization.

Experiments involving the mechanical motion of 1/4-inch carbon; thin, composite; and metal electrodes have been completed at frequencies ranging from 20 to 300 c. p. s. In no instance did the cell voltage change by more than several millivolts as a result of the vibrations. Experiments involving the sonic pulsing of electrolyte did not reveal any significant effects on cell performance resulting from the pulsations. Author

3.0 MEETINGS AND CONFERENCES

On February 13, 1964, K. V. Kordesch and M. L. Kronenberg of Union Carbide visited the laboratories of Professor T. J. Gray at Alfred University. The purpose of the visit was to observe how Professor Gray prepared metal electrodes so that the results of pulsing experiments from the two laboratories could be compared on the same type of hydrophilic electrodes.

4.0 FACTUAL DATA

4.1 Electrical Pulsing.

In addition to the 60 cycles/sec. interrupted d. c., 6 sec. /cycle interrupted d. c., and discharging-charging cycles described in the 2nd Quarterly Report the following types of pulsing experiments were carried out: 300 cycles per second interrupted d. c.; a. c. from 20 to 20,000 c. p. s. superimposed on d. c.; and short, high-discharge pulsing. These pulsings have been performed on 1/4-inch and on thin, composite electrodes thus far, and are presently being tried on metal electrodes.

4.1.1 300-Cycles/Second Interrupted D. C.

The circuit used to obtain the interrupted d. c. is shown in Fig. 1. The magnitude and wave form of the resulting current as shown in Fig. 2 was obtained by feeding the voltage across a 1-ohm precision resistor into a 535A oscilloscope. A control cell run with continuous d. c. was run at the same time as each test cell on interrupted d. c. For both the 1/4-inch and the thin, composite electrodes there was no significant difference between the polarization curves for the control cells and the test cells after several days continuous operation at 50 ma/cm^2. The tests were terminated after this period to make room for new cells. In Fig. 3 performance curves are shown for 1/4-inch carbon electrode control and test cells after 6 days of continuous operation. The difference in performance of several millivolts between the control cell and the test cell is not regarded as significant.

4.1.2 A. C. from 20 to 20,000 C. P. S. Superimposed on D. C.

Pulsing experiments involving a. c. superimposed on d. c. over the range 20 to 20,000 c. p. s. were conducted using 1/4-inch carbon and thin, composite electrodes. The cells (electrode area = 2 cm^2) were run at 50 ma d. c. with superimposed a. c. of 10 or 25 ma, and at 100 ma d. c. with superimposed a. c. of 10 or 25 ma. A HP-201B Hewlett-Packard sine wave signal generator was used and the current wave form and frequencies were observed over the 20 - 20,000 c. p. s. range with a Tektronix 535-A oscilloscope. A diagram of the circuit used is shown in Fig. 4 and the wave form for 50 ma d. c.

with superimposed a. c. of 10 ma at 1000 c. p. s. is shown in Fig. 5 as an example of the wave forms observed on the oscilloscope.

The cell voltage for 1/4-inch carbon electrodes held constant at 0. 873 volt (IR-free) at currents of 50 ma d. c., 10 ma a. c., and 50 ma d. c., 25 ma a. c., while the frequency of the a. c. component was varied from 20 to 20, 000 c. p. s. At 100 ma d. c., 10 ma a. c. and 100 ma d. c., 25 ma a. c. the voltage held at 0. 782 (IR-free) while the frequency of the a. c. component was varied over the same range. The experiments were repeated for IR-included potentials and these also did not vary even 1 mv over frequency ranges noted above. Thin, composite electrodes showed the same potential invariance with frequency.

4. 1. 3 Effect of Heavy Discharge Pulsing.

It was noted by K. V. Kordesch that a short, heavy discharge pulse often improved the performance level of these electrodes significantly above that obtained by continuous discharge. A systematic study of this effect has begun; thus far, the following observations have been made:

(1) The effect has been especially pronounced on thin, composite electrodes;

(2) The effect has been observed primarily at the anode and in general is most pronounced for anodes with more than 100 mv polarization;

(3) The most effective results were obtained when the anode-reference potential (vs. zinc) was driven to 1. 2 - 1. 8 volts by a discharge pulse of 1 - 3 seconds duration applied every few minutes. (This is in the vicinity of the oxygen electrode potential.)

The effect can best be described by reference to experimental data as shown in Fig. 6. The discharge current density is 75 ma/cm^2 and the heavy pulse current density is 350 ma/cm^2. The recorder here was set at zero center and 2000 mv full scale. Each cycle represents approximately 2 minutes, including the 2-second heavy discharge pulse. At point "A" the cell voltage is 0. 8 volt and decays to 0. 76 volt under the 75 ma/cm^2 load after about 2 minutes (point "B"). The 2-second heavy discharge pulse drives the cell voltage to approximately -0.5 volt (point "C") after which the cell voltage recovers to 0.80 volt (point "D"), or 40 mv higher than before the heavy-pulse discharge. The cell voltage later decreased to a failure point when left on continuous load. In Fig. 7 an even greater effect of heavy discharge pulsing is shown on another cell. After the 1-second heavy discharge pulse (500 ma/cm^2), the cell voltage recovered about 100 mv over where it left off (normal load 150 ma/cm^2, recorder set at 1000 mv full scale). At point "A" the normal discharge was continued for several minutes without heavy discharge pulsing. The cell voltage decreased to 0.53 volt then recovered to an average of 0.68 volt when pulsing was resumed. In Fig. 8 is pictured more than an hour's data from the same cell run at 100 ma/cm^2 and maintained at an average potential of 0.76 volt by heavy discharge pulsing. The recorder speed is 6 inches/hour.

We believe the phenomena described above is related to catalyst reactivation but feel that the results are too preliminary to justify an extensive interpretation at this time.

4.2 Mechanical Motion of Electrodes.

Vibration tests were conducted on all three types of electrodes in three different ways: by coupling the plunger of a continuous-duty solonoid directly to the electrode backing plate and driving at 60 cycles by means of Variac; by mounting on a light vibration table and vibrating the complete cell at several different amplitudes in the range of 20 to 200 c.p.s. by means of a signal generator and power amplifier; and by mounting the cell on a support driven by a compressed-air driven vibrator which vigorously vibrates in the range of 160 - 300 c.p.s. In no instance did the resistance-free or resistance-included cell voltage change by more than several millivolts for 1/4-inch, thin-composite, or metal electrodes over these frequency ranges. Resistance-free cell voltages at constant current for each type of electrode is shown in Fig. 9. The thin, composite electrodes exhibited the greatest "breaking-in" voltage fluctuations.

4.3 Sonic Pulsing.

Experiments involving the sonic pulsing of electrolyte have been completed for 1/4-inch and thin, composite electrodes. A picture of the experimental setup and equipment used is shown in Fig. 10. A diaphragm at the bottom of the Teflon cell (1) is vibrated by means of an audio-driver unit (2). A signal generator

(3) and amplifier (4) provide frequency control and power to the driver unit. The pressure fluctuations are sensed by a transducer (5) which is excited by another signal generator (6). Pressure fluctuations are read on the oscilloscope (7) as voltage readings.

Tests have been run at frequencies ranging from 20 to 20,000 c.p.s. at two pressure amplitudes for 1/4-inch carbon and thin, composite electrodes. For both types of electrodes, no significant changes in cell voltages were noted over this frequency range, as shown in Fig. 11. The transducer was not fast enough to follow the pressure fluctuations at high frequencies but experimental verification of electrolyte pulsing at sonic frequencies was obtained.

5.0 FUTURE WORK

The work during the next period will be concerned with applying the electrical, mechanical and sonic pulsing experiments already performed on 1/4-inch carbons and the thin, composite electrodes to metal electrodes. Any significant results of pulsing are more likely to appear on these hydrophilic electrodes than on the nonwetting types tested thus far.

The improvements resulting from short, heavy discharge pulses will be investigated in more detail on thin, composite and metal electrodes. A special pulsing circuit is being designed and constructed to control the duration and intensity of the pulses.

M. L. Kronenberg

jdh

M. L. Kronenberg
Project Leader

APPENDIX

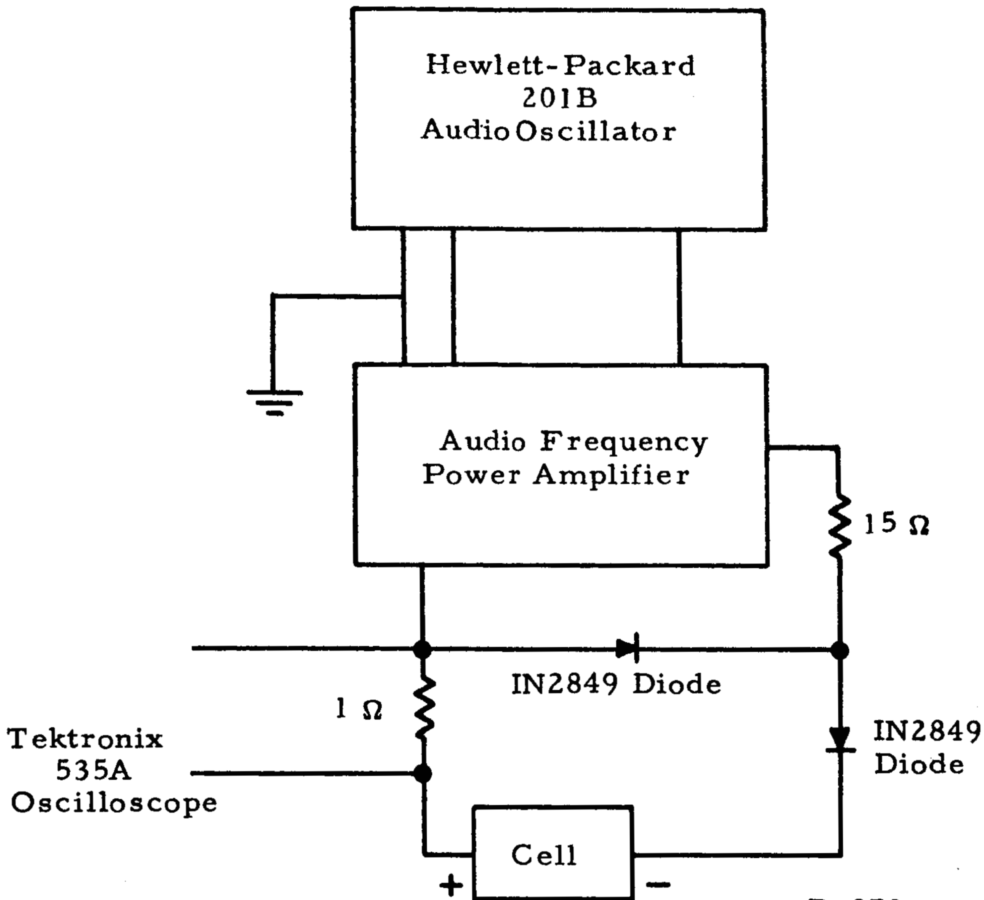

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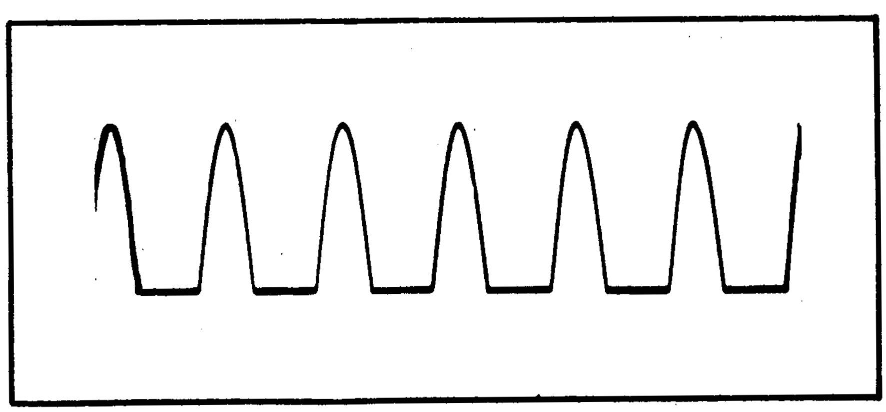
Fig. 1 Circuit Used for Interrupted D. C.



D-867

Fig. 2 Interrupted D. C. Wave Form.
(300 c. p. s., Avg. Current 100 ma)

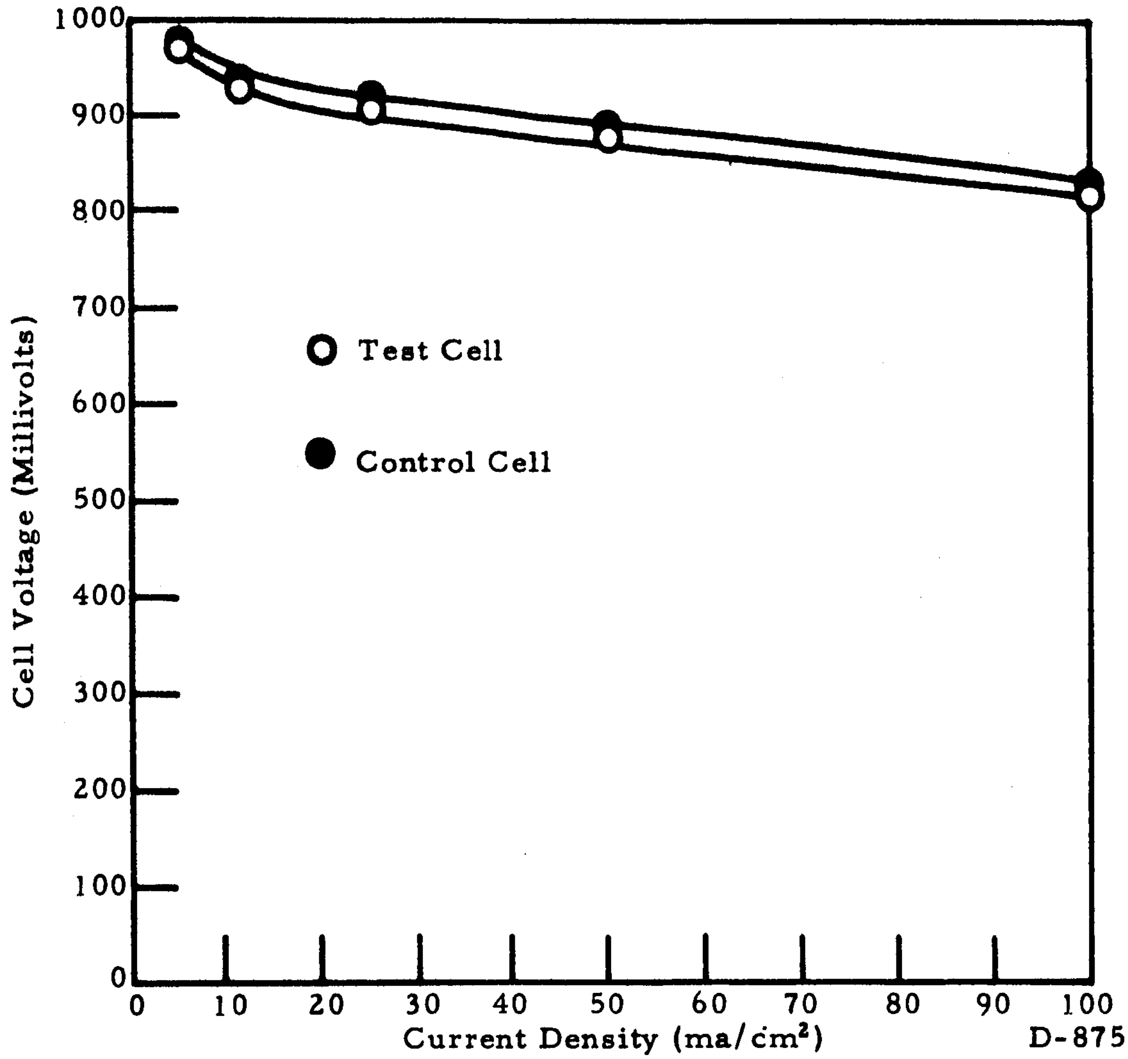


Fig. 3 Performance Data for Cell Run on Continuous D. C. in Comparison with One Run at 300 C. P. S., Pulsed D. C.

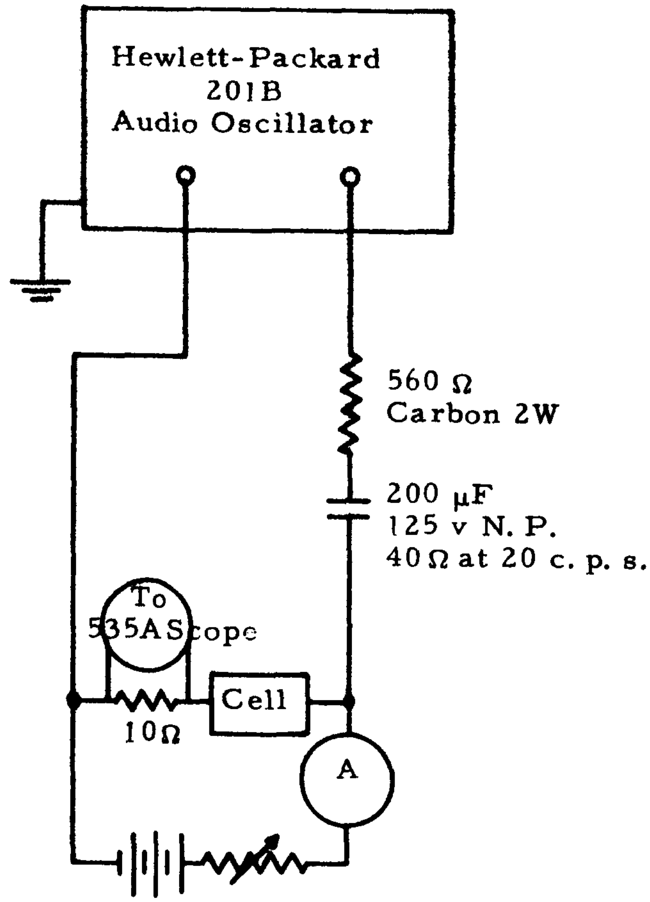


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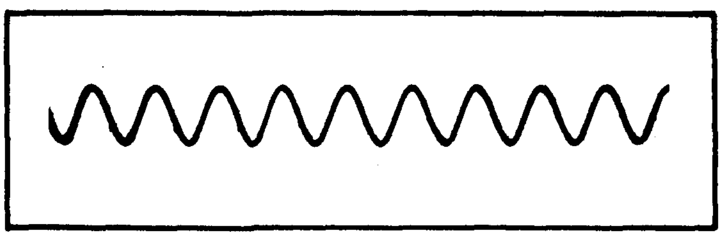
Fig. 4 Circuit Diagram for A. C. Superimposed on D. C.



D-868

Fig. 5 Wave Form of A. C. Superimposed on D. C. - 50 ma D. C., 10 ma Superimposed A. C. - (1000 c. p. s.) - 200 mv/cm. Sweep Time = 1 millisec. /cm.

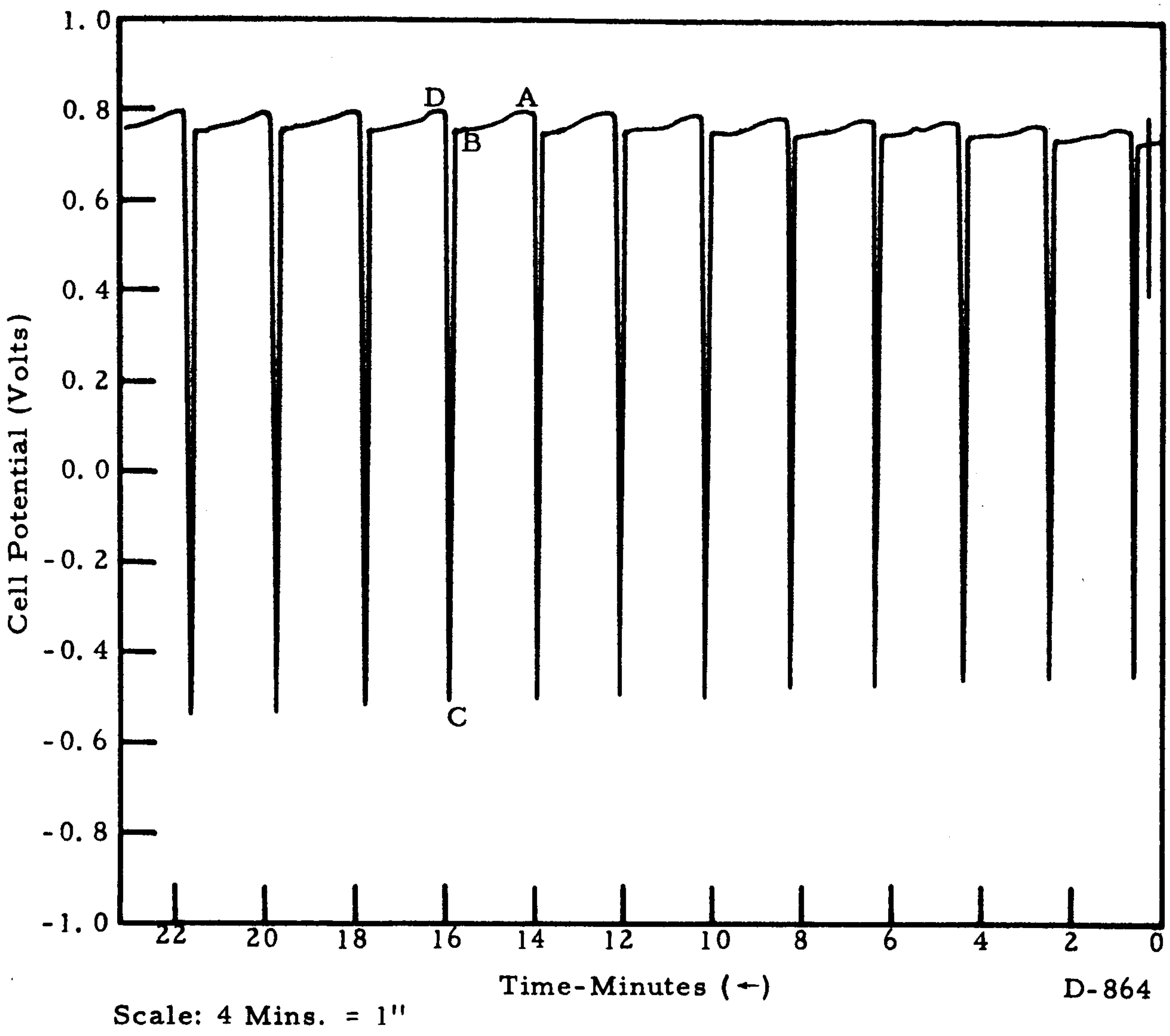


Fig. 6 Effect of Heavy Discharge Pulse on Cell Voltage

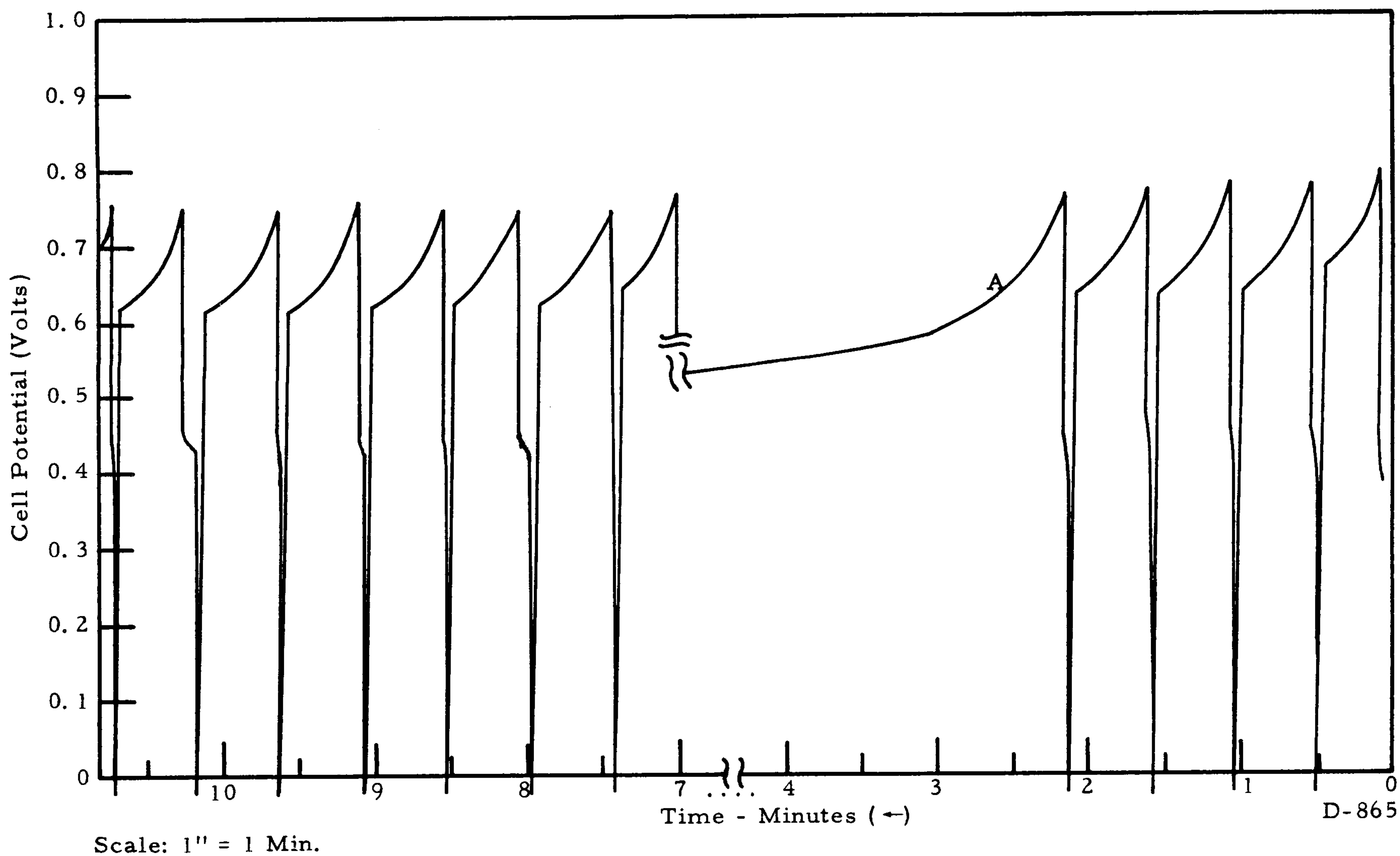
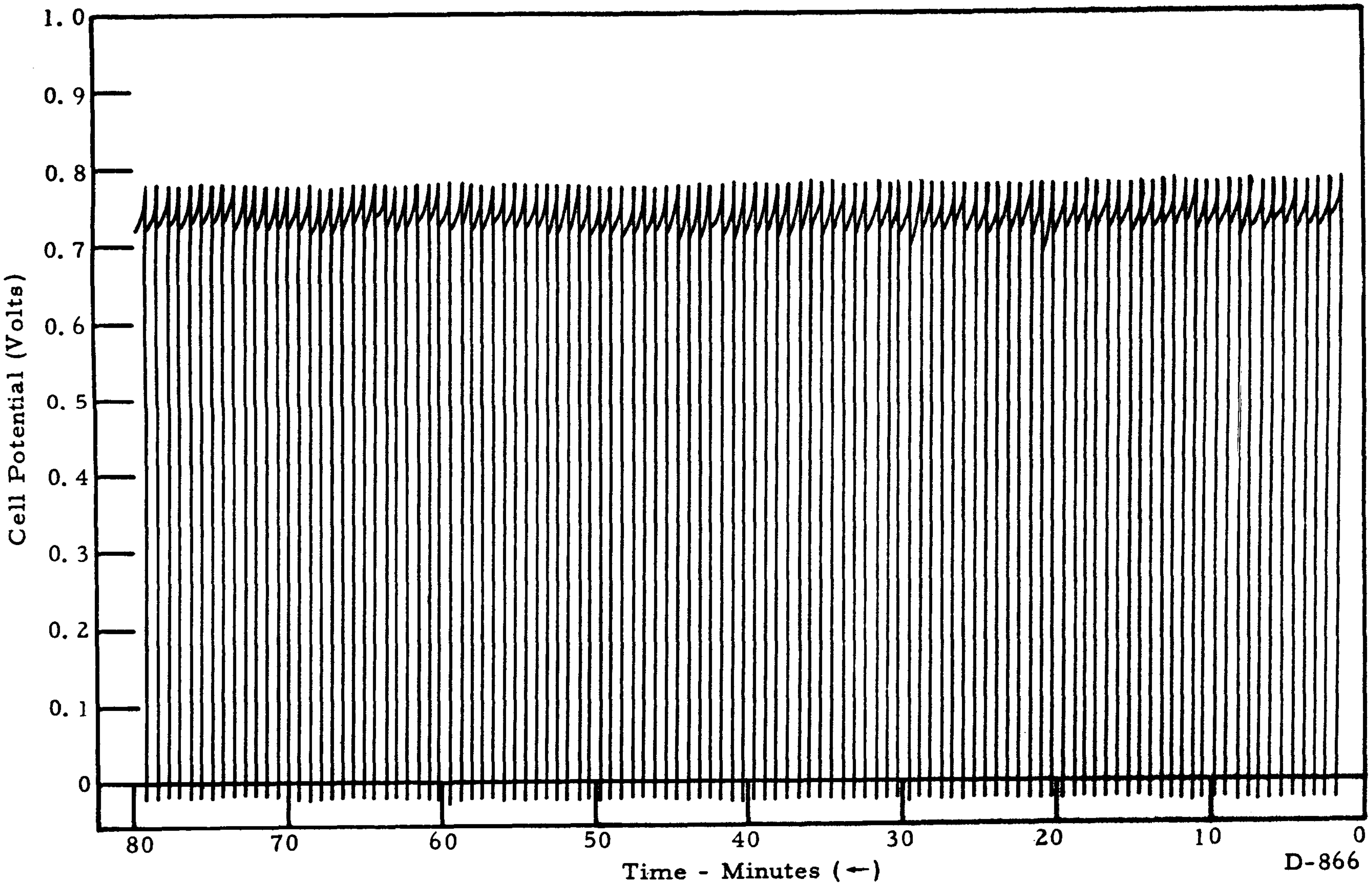


Fig. 7 Comparison Heavy Discharge Pulse and Normal Discharge.



Scale: 1" = 10 Mins.

Fig. 8 Cell Voltage Maintained by Heavy Discharge Pulse.

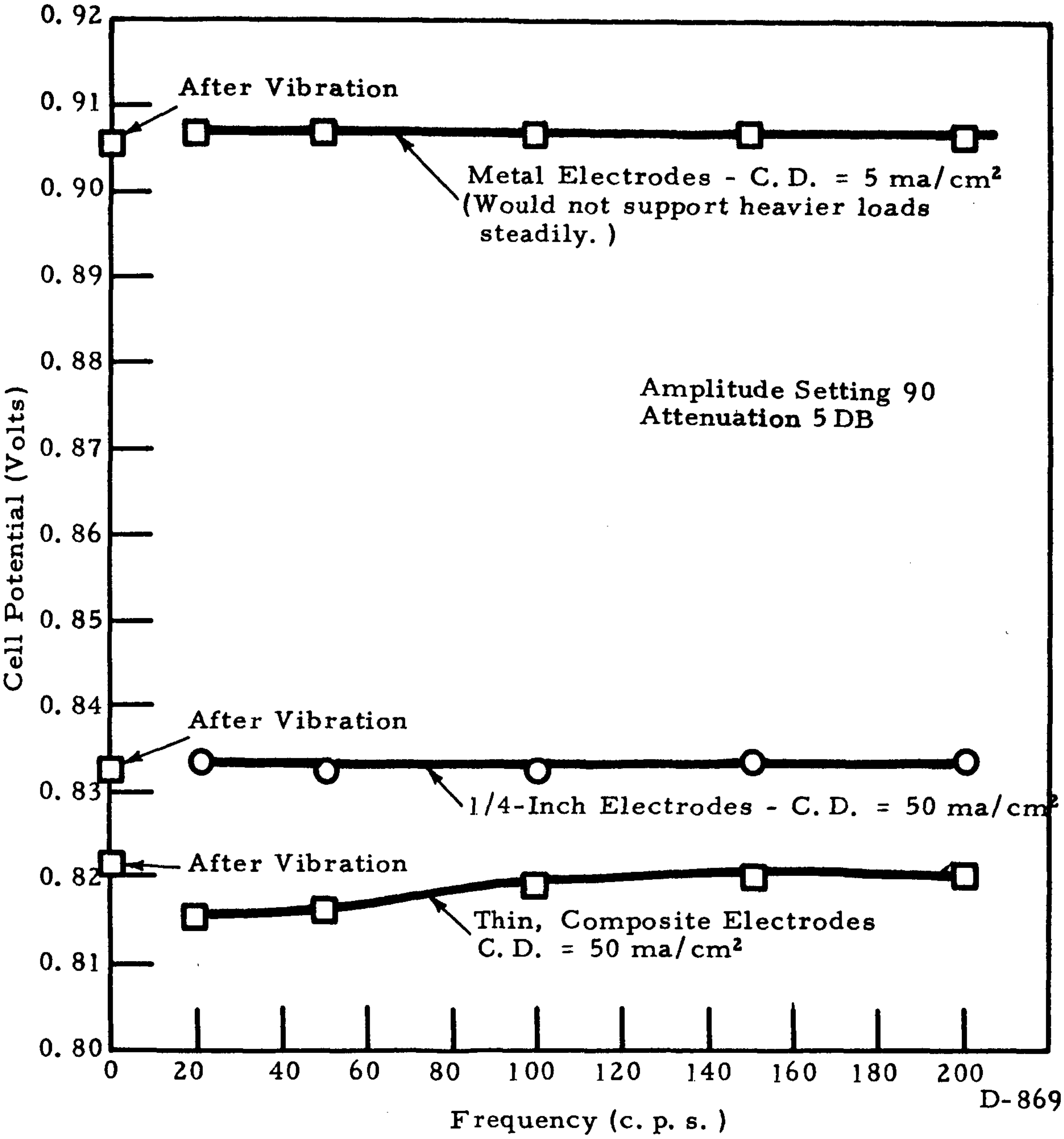


Fig. 9 Cell Voltage vs. Vibration Frequency for Three Types of Electrodes.

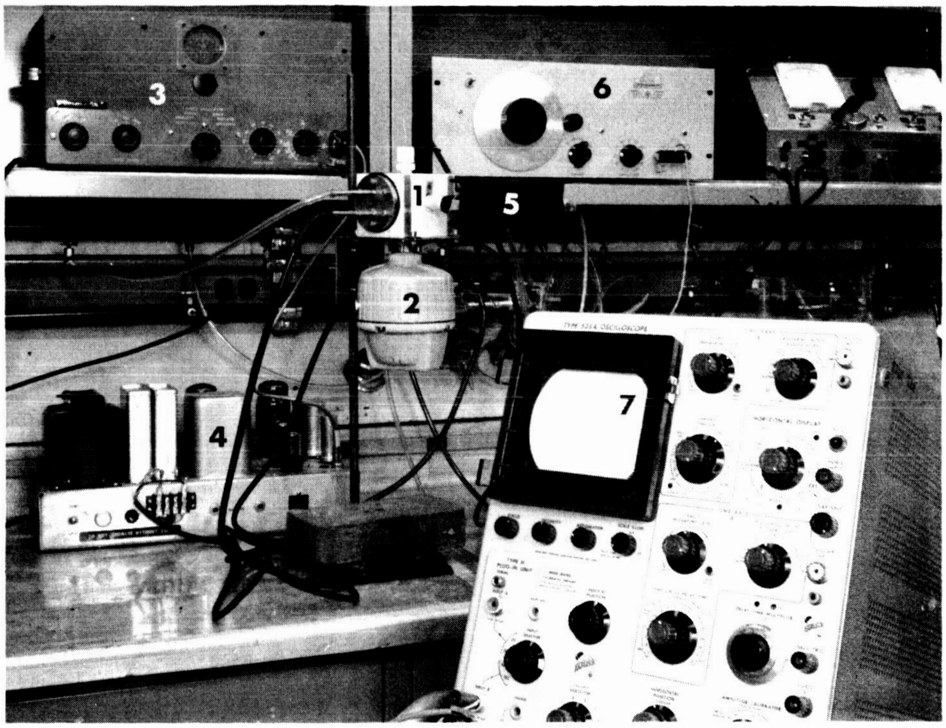


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Fig. 10 Equipment for Sonic Pulsing of Electrolyte

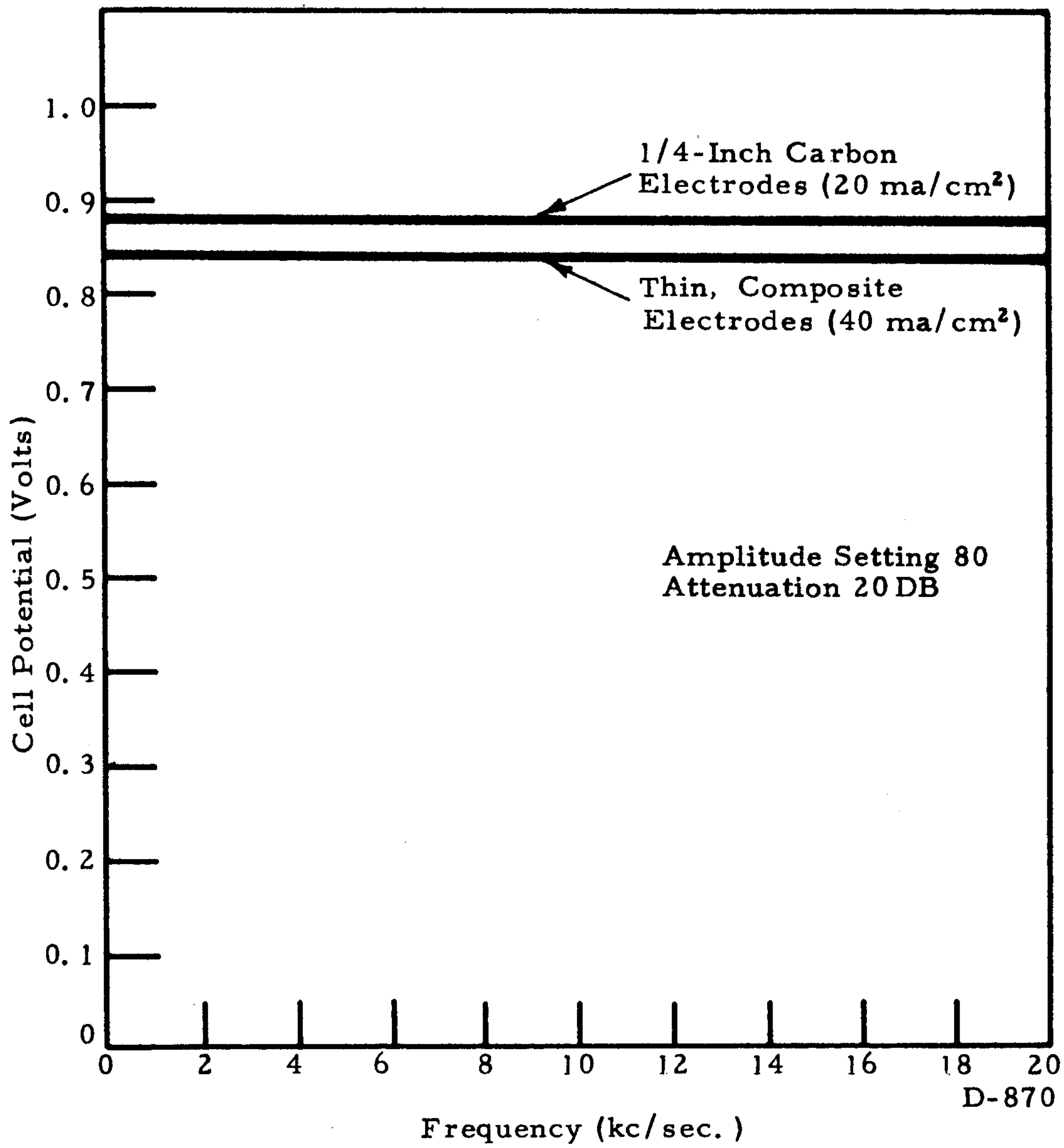

Fig. 11 Effect of Electrolyte Pulsations on Cell Voltage for 1/4-Inch Carbon and on Thin, Composite Electrodes.

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